



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US95/00291 <b>(22) International Filing Date:</b> 9 January 1995 (09.01.95) <b>(30) Priority Data:</b> 08/179,157 10 January 1994 (10.01.94) US <b>(71) Applicants:</b> LIBBEY-OWENS-FORD CO. [US/US]; 811 Madison Avenue, Toledo, OH 43697 (US). PILKINGTON GLASS LIMITED [GB/GB]; Prescot Road, St. Helens, Merseyside WA10 3TT (GB). <b>(72) Inventors:</b> GOODMAN, Ronald, D.; 3618 W. Lincolnshire Boulevard, Toledo, OH 43606 (US). SOUBEYRAND, Michel, J.; 7935 North Shoreline Drive, Holland, OH 43528 (US). JENKINSON, Timothy; 3 Ash Close, Appley Bridge, Wigan, Lancashire WN6 9HU (GB). <b>(74) Agent:</b> OBERLIN, Phillip. S.; Marshall & Melhorn, Four SeaGate, 8th floor, Toledo, OH 43604 (US).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COATINGS ON GLASS		
<b>(57) Abstract</b>  A method of producing mirrors comprising depositing onto a ribbon of hot glass during the production process a coating comprising at least one pyrolytic reflecting layer and at least one color modifying layer whereby the mirrors exhibit color in reflectance and have a visible light reflection of at least 35 % and less than 70 %. There is also provided a mirror having such a coating.		

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TITLE  
COATINGS ON GLASS

CROSS REFERENCE TO RELATED APPLICATIONS

5        This application is a continuation-in-part of United States application Serial No. 08/087,329, filed July 8, 1993. This latter application shows the following foreign application priority data:

      July 11, 1992 [GB] United Kingdom ..... 9214766.9  
10       April 30, 1993 [GB] United Kingdom ..... 9309036.3

BACKGROUND OF THE INVENTION

      The invention relates to a method of producing mirrors, and to coated glass substrates incorporating  
15       coatings exhibiting reflected color.

      The light reflecting properties of mirrors are generally provided by a layer of highly reflecting metal, especially silver, aluminum or chromium, applied to a glass or plastics substrate; copper layers are sometimes  
20       used as an alternative, but are generally less acceptable because of the strong red tint of the reflected light.

      Silver coatings are generally applied to preformed glass plates, in the cold, by wet chemical methods in which a solution of silver salt is applied to the glass  
25       surface and reacted with a reducing agent which reduces silver ions present to silver metal which deposits on the glass surface. The silver used is not very durable in use and in practice requires protection by other layers, and these methods are generally unsuitable for application to  
30       glass on the production line on which it is formed so that a separate "silvering" line is required to produce the silvered glass.

      Aluminum coatings are difficult to apply by chemical methods because of the strongly reducing nature of

aluminum metal, and aluminum mirrors are generally produced by deposition methods carried out at low pressure, e.g., by sputtering. Such low pressure methods are essentially batch processes and, like the wet chemical  
5 methods used for deposition of silver mirrors, are generally unsuitable for on-line application on the production line on which the glass is made.

Silicon layers have also been used to produce reflecting layers (which, like silver and aluminum layers,  
10 are substantially neutral in reflection color) on architectural glazing for aesthetic and solar control purposes. U.S. patents Nos. 4,088,471, 4,188,444 and 4,469,045 relate to a continuous chemical vapor deposition method for producing float glass having such a silicon  
15 layer, and U.S. patent 4,661,381 describes a development of that method.

#### SUMMARY OF THE INVENTION

The present inventors have discovered that coatings  
20 can in practice be applied on-line to glass during the production process, especially on a float glass production line, to produce mirrors particularly adapted for automotive use and even more beneficially for outside automotive mirrors, i.e., side view mirrors, having a  
25 visible light reflection in the range of at least 35% to less than 70% and a reflected color. Preferably, the mirrors will have a visible light reflection between 35% and 60% and most preferably between 35% and 55%. The reflected color, which results from a unique combination  
30 of layer compositions and thicknesses, will generally be such that, when defined by reference to the CIELAB color scale system,  $a^2+b^2$  is greater than 50 and preferably

greater than 100 [Illuminant A]. Reflection colors in the blue-green sector (that is,  $a^*$  and  $b^*$  both negative) are preferred, and in a particularly desired product the reflected color has the following values:  $a^*$  between -10, preferably between -15, and -25 and  $b^*$  between -15 and -30 (Illuminant A).

According to the present invention there is provided a method of producing mirrors having a colored visible light reflection of less than 70%, including depositing onto a ribbon of hot glass during the production process a coating comprising at least one pyrolytic layer and at least one color modifying layer. The coated ribbon is cut on-line, and will usually be further cut and bent off line to provide separate mirrors of the required size and shape.

The pyrolytic layer is a light reflecting layer and is, in use, furthest from the source of light to be reflected, and the color modifying layer or layers are between the light source and the reflecting layer. Thus, for front surface mirrors the inner of the said layers is the reflecting layer and intermediate and outer layers act as color modifying layers, with the outer layer also taking on a protective layer status or function. The inner layer is identified as the layer of the coating nearest to the glass and the outer layer as the layer furthest from the glass of all the layers.

It is known in the art that refractive index varies with wavelength. In this specification and claims, references to "refractive index" are intended to mean (in conventional manner) the refractive index for light of wavelength 550 nm and, in assessing and quoting refractive

index values, any imaginary part of the refractive index is disregarded.

The expression "visible light reflection", as used in the present specification and claims, refers to the percentage of light reflected under Illuminant D65 source 1931 Observer Conditions.

The reflecting layer should have a relatively high refractive index and the color modifying layer or layers should be of lower refractive index. The precise refractive indices required will depend on the light reflection to be achieved, and for a visible light reflection of around 35%, the reflecting layer should have a refractive index of above 2, preferably at least 2.5. For higher light reflections, high refractive indices will be desirable so that, for a visible light reflection of 60%, a material of refractive index of at least 2.8 will generally be used for the reflecting layer. The color modifying layer or layers will usually have a refractive index less than 2.

Silicon is preferably used for the pyrolytic reflecting layer because (a) it is readily deposited on-line on hot glass, for example, by the processes described in U.S. patents Nos. 4,088,471, 4,188,444 and 4,469,045, and (b) provides a visible light reflection in the range of at least 35% to less than 70% in readily obtainable thicknesses of 100Å to 300Å.

The refractive index of silicon may be as great as about 5, (see P.J. Martin, R.P. Netherfield, W.G. Sainty and D.R. McKenzie in Thin Solid Films 100 (1983) at pages 141-147) although lower values are often encountered.

It is believed that, in practice, the value varies depending on the precise physical form of the silicon and

the presence of any impurities, for example oxygen, nitrogen or carbon. For the purpose of the present invention, the presence of such impurities may be tolerated (and indeed, it is difficult in practice to produce on-line silicon coatings without significant oxygen and/or carbon incorporation) provided the refractive index is not reduced below about 2.8. Thus the term "silicon" as used herein refers to material which is predominantly silicon, but may contain minor proportions of impurities, provided its refractive index is at least 2.8.

While its high refractive index and ease of deposition favor the use of silicon, other materials may be employed as the reflecting layer.

It is preferred to use as an intermediate color modifying layer a material which can be pyrolytically deposited and has a refractive index less than 2. A suitable and convenient layer material is silicon oxide, which may however contain trace amounts of elements such as carbon or nitrogen, and the term "silicon oxide" is used herein to encompass silicon oxides containing these trace elements having a refractive index of less than 2. Surprisingly, it is found in practice, that adjacent layers of silicon and silicon oxide can be applied pyrolytically to the glass without interdiffusion or interactions which would cause unacceptable reduction in the refractive index of the silicon or increase in the refractive index of the silicon oxide; the adjacent layers of silicon and silicon oxide appear to remain, at least in terms of their optical performance, separate and distinct. However, it may be that at the interfaces of the layers there exist physically narrow interaction zones with steep

refractive index gradients that do not alter the optical characteristics of the mirror.

In order to achieve the desired reflection and color properties, the intermediate color modifying layer should  
5 have a thickness in the range of 100Å to 400Å, preferably 200Å to 400Å.

Another material which may be used for the intermediate layer is aluminum oxide.

The outer layer of the mirror coating of the  
10 invention influences the reflected color and provides a protective layer for the reflecting and color modifying layers. Suitably, the outer layer may be tin oxide, titanium oxide, or mixtures thereof in a thickness range of 500Å to 1000Å. This layer, similarly to the  
15 intermediate color modifying layer(s) will normally have a refractive index of no more than 2, although titanium oxide may have a refractive index of up to 2.4. Preferably, the layer is undoped tin oxide in a thickness between 750Å and 1000Å and has a refractive index of  
20 approximately 1.9.

According to the method of the invention, the layers of the required index and thickness are applied to a ribbon of hot glass during the glass production process. The depositions may be carried out in a known manner by  
25 liquid or powder spray processes, or by a chemical vapor deposition process, and each of the layers may be deposited by a different type of process. The depositions may be pyrolytic involving decomposition of a compound which is a precursor for the material of the desired  
30 layer, possibly by reaction with another compound.

In general, it is convenient to use a chemical vapor deposition process to apply any silicon or silicon oxide



(which may contain carbon) layers that may be required. Thus, for example, any silicon layer may be deposited (directly or indirectly) on the hot substrate by chemical vapor deposition from a silane gas, conveniently in an  
5 inert gaseous diluent or carrier gas, for example nitrogen and/or helium. It is generally most convenient to use monosilane, although other silanes may also be used, such as dichlorosilane. One suitable process for deposition of such a silicon layer is described in U.S. patent No.  
10 4,188,444. If desired, for example to improve the alkali resistance of the silicon coating, the reactant gas may contain a proportion of a gaseous electron donating compound, especially an ethylenically unsaturated hydrocarbon compound, for example, ethylene, as an  
15 additive.

A silicon oxide layer for use as the color modifying layer of low refractive index (i.e., an intermediate layer) may similarly be deposited by chemical vapor deposition from a silane gas, conveniently in a gaseous  
20 inert diluent or carrier gas, in admixture with oxygen or a source of oxygen. It is preferred to use a mixture of a silane and an ethylenically unsaturated hydrocarbon, e.g., ethylene, together with oxygen gas. The relative concentrations of silane and the source of oxygen used  
25 will depend on the refractive index required; in general, the lower the refractive index required, the larger the proportion of oxygen-containing compound to silane to be used. Again, the silane used is preferably a monosilane.

For a metal oxide outer layer, such as tin oxide or  
30 titanium oxide, either a liquid or powder spray process or a chemical vapor deposition procedure will generally be used. Thus, for example, a layer of tin oxide or titanium

oxide may be deposited by chemical vapor deposition by reaction of the corresponding gaseous metal chloride and water vapor, or by spraying a non-aqueous solution of the metal chloride onto the hot glass in the presence of water vapor. Thus, tin oxide may be deposited by chemical vapor deposition of components selected from tin tetrachloride and water vapor, and an organo tin compound such as diethyl tin dichloride or tetramethyl tin, and oxygen, the oxygen optionally being present in air. The titanium oxide may be deposited by chemical vapor deposition of a titanium alkoxide, such as titanium isopropoxide, optionally in the presence of water or air. Preferably, undoped tin oxide is the outer protective layer and is deposited by chemical vapor deposition from a gaseous precursor mixture composed of an organometallic compound such as dimethyl tin dichloride, water vapor, oxygen and helium.

When applying a coating layer to a ribbon of float glass, the chemical vapor deposition techniques can conveniently be carried out inside the float bath, i.e., where the glass is supported on a molten metal bath under a protective atmosphere (but preferably after the glass has finished stretching, i.e., at a glass temperature below 750°C), or after the ribbon has emerged from the float bath. When using a gas containing monosilane to deposit silicon or silicon oxide layers, it is preferred to carry out the deposition of that layer in the float bath where the glass is at a temperature in the range of 600°C to 750°C in order to achieve a satisfactory rate of deposition.

When applying a coating layer to a ribbon of float glass by a liquid or powder spray process, it will

generally be more convenient to deposit the layer after the ribbon of glass has emerged from the float bath.

As previously noted, the process of the present invention is useful for the production of automotive mirrors, particularly outside side view mirrors. The mirrors may be provided with an obscuring layer, preferably a substantially opaque layer, on the side which is to be remote from the source of light to be reflected in use. Thus, for front surface mirrors the obscuring layer will generally be applied over the uncoated back surface of the glass.

The ability to produce glass mirrors on-line at high yield, using coating steps based on known technology, for example the pyrolytic deposition of a silicon layer, is an important step forward and many important mirror products which may be produced in this way are novel.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated but not limited by the following drawings and Examples. In the drawings:

Figure 1 is a perspective view, with parts broken away, of a mirror in accordance with the invention in use as a front surface outside automotive mirror.

Figure 2 is a diagrammatic representation of the arrangement of coating stations on a float glass production line for production of mirrors in accordance with the method of the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Figure 1, a front surface glass outside automotive mirror is shown assembled in a suitable casing 10 and comprises a float glass substrate 12 carrying a

coating 14 comprising an inner layer 16 of relatively high refractive index, for example of pyrolytic silicon having a refractive index of at least 2.8, an intermediate layer 18 of relatively low refractive index, for example of silicon oxide having a refractive index below 2, and an outer layer 20 of, for example of pyrolytic tin oxide.

All of the layers are applied by chemical vapor deposition. The reflective layer 16 has a thickness in the range of 100Å to 400Å, the color modifying layer 18 a thickness in the range of 200Å to 400Å, and the outer protective layer 20 a thickness in the range of 500Å to 1000Å.

Figure 2 illustrates diagrammatically, a float glass production line comprising a glass melting section 30, a float bath section 32 for forming the molten glass into a continuous ribbon, a lehr section 34 for annealing the glass ribbon, a wareroom section 36 for cutting pieces of glass from the ribbon for storage and/or distribution and use, and a bending and tempering station 38. For the production of mirrors in accordance with the method of the invention, each of the three coating stations for respectively applying the inner, intermediate and outer layers will normally be located in or between the float bath section 32 and lehr section 34; in the illustrated embodiment of the invention, the three coating stations 40, 42, 44 are arranged in the float bath section 32 as shown in Figure 2. However, in alternative embodiments, one or each of the coating stations for applying inner, intermediate and outer layers in accordance with the invention may be located between the float bath section 32 and the lehr section 34. The location of each coating station is selected to be at a position where the glass

ribbon has substantially reached its final thickness (usually at a glass temperature of around 750°C) so that it is not subject to further stretching which might crack any coating applied, but where its temperature remains  
5 sufficiently high for formation of a further pyrolytic layer (usually a glass temperature of at least 300°C).

The following Examples illustrate the present invention without limiting it, and in the Examples mirrors were produced on-line using a float glass production line  
10 having the structure shown in Figure 2.

#### Examples

Glass mirrors, intended for use as front surface mirrors, were produced using the laminar vapor coating  
15 process and apparatus described in U.S. patent No. 4,504,526. Three separate coating beams, each as described in this patent, were used to apply successive silicon, silicon oxide and tin oxide layers (Examples 1 and 3) and silicon, silicon oxide and silicon layers  
20 (Example 2) to a ribbon of float glass having a thickness and advancing at a Lehr speed shown in Table 1. Each of the three coating beams was located in the float bath where the glass ribbon was supported on a bath of molten metal. The upstream, intermediate and downstream (each  
25 with reference to the direction of glass advance) beams were each respectively located at positions where the glass temperature was approximately as specified in Table 1.

The beams had a coating chamber with a length of  
30 approximately 40 cm in the direction of glass advance.

The upstream, intermediate and downstream beams were each fed with the respective gas mixtures specified in

Table 1. Nitrogen ( $N_2$ ) and helium (He) were used as carrier gases. In these Examples, the gas flows were all measured at ambient temperature and pressure 1 bar, except for flows of dimethyl tin dichloride (DMT) and water which  
5 are measured as a liquid, and all are quoted per metre width of glass coated.

No modification of the lehr conditions was required to anneal the resulting coated ribbon which had a reflecting appearance, the reflection being blue in color.  
10 The color can be quantified by the use of the CIELAB color coordinate system which is well known to the person skilled in the art. Examination of sample mirrors cut from the ribbon showed them to have a visible light reflection and color coordinates as specified in Table 2.  
15 In the Examples, the reflection and the color coordinates were measured using Illuminant D65 source 1931 Observer conditions. The measurements were on the coated side of the glass.

The thickness and refractive index of the individual  
20 layers of the coating were estimated from the reflection spectra of the individual layers deposited separately and the estimated values are specified in Table 2.

Several of the samples were bent to large radii of curvature on the order of 40 to 60 inches. These  
25 curvatures are those which would normally be found in outside automotive mirrors. No deterioration in physical appearance or reflective properties was observed.

TABLE 1

	Glass Thickness mm	Glass Speed m/hour	Upstream Beam Temp. °C Gas Flows litres/min	Intermediate Beam Temp. °C Gas Flows litres/min	Downstream Beam Temp. °C Gas Flows litres/min
Example 1	2.3	820	710 SiH <sub>4</sub> :2.9 N <sub>2</sub> :26 He:115	680 SiH <sub>4</sub> :1.7 C <sub>2</sub> H <sub>4</sub> :17 O <sub>2</sub> :3.6 N <sub>2</sub> :63 He:57	600 DMT:10.3 lbs/hr H <sub>2</sub> O:13.2 lbs/hr O <sub>2</sub> :200 He:300
Example 2	1.2	320	680 SiH <sub>4</sub> :0.3 N <sub>2</sub> :40	630 SiH <sub>4</sub> :2.8 C <sub>2</sub> H <sub>4</sub> :0.4 N <sub>2</sub> :25 *CH <sub>3</sub> COCH <sub>3</sub> :9.4	620 SiH <sub>4</sub> :1.1 C <sub>2</sub> H <sub>4</sub> :0.2 N <sub>2</sub> :20
Example 3	2.3	820	710 SiH <sub>4</sub> :4.6 N <sub>2</sub> :26 He:115	680 SiH <sub>4</sub> :1.1 C <sub>2</sub> H <sub>4</sub> :17 O <sub>2</sub> :3.6 N <sub>2</sub> :63 He:57	600 DMT:10.3 lbs/hr H <sub>2</sub> O:13.2 lbs/hr O <sub>2</sub> :200 He:300

\* mls/min

TABLE 2

	Reflection	a*	b*	Inner Layer Thickness nm	Intermediate Layer Thickness nm	Outer Layer Thickness nm	Ref Index
Example 1	47%	-24.2	-21.3	20	30	80	1.90
Example 2	47%	-21.5	-16.8	N/A	N/A	N/A	4.6
Example 3	48%	-17	-15	27	21	80	1.90

In accordance with the provisions of the patent statutes, the present invention has been described in what is considered to represent its preferred embodiment. However, it should be noted that the invention can be  
5 practiced otherwise than as specifically illustrated and described without departing from its spirit or scope.



## WHAT IS CLAIMED IS:

1. A method of producing mirrors including depositing onto a ribbon of hot glass during the production process a coating comprising at least one pyrolytic reflecting layer and at least one color modifying layer, whereby the mirrors exhibit color in reflectance and have a visible light reflection of at least 35 and less than 70%.
2. A method of producing mirrors as defined in claim 1, wherein said coating exhibits a color as defined by the CIELAB color scale system of  $a^*$  between -10, preferably between -15, and -25 and  $b^*$  between -15 and -30 (Illuminant A).
3. A method of producing mirrors as defined in claim 2, wherein said mirrors have a visible light reflection in the range of 35% to 60%, preferably, 35% to 55%.
4. A method of producing mirrors including depositing onto a ribbon of hot glass during the production process a coating comprising a pyrolytic reflecting layer, a color modifying layer, and a protective layer, whereby the mirrors exhibit color in reflectance and have a visible light reflection of less than 70%.

5. A method of producing mirrors as defined in claim 4, wherein said coating exhibits a color as defined by the CIELAB color scale system of  $a^*$  between -10, preferably between -15, and -25 and  $b^*$  between -15 and -30 (Illuminant A).

6. A method of producing mirrors as defined in claim 5, wherein said pyrolytic reflecting layer comprises silicon and has a refractive index of at least 2.8.

10

7. A method of producing mirrors as defined in claim 6, wherein said silicon layer has a thickness in the range of 100Å to 300Å.

15

8. A method of producing mirrors as defined in claim 5, wherein said color modifying layer comprises an oxide of silicon having a refractive index of less than 2.

9. A method of producing mirrors as defined in claim 8, wherein said oxide of silicon has a thickness in the range of 100Å to 400Å.

10. A method of producing mirrors as defined in claim 9, wherein said oxide of silicon has a thickness in the range of 200Å to 400Å.

11. A method of producing mirrors as defined in claim 5, wherein said protective layer comprises an oxide selected from the group consisting of tin oxide, titanium oxide and mixtures thereof in a thickness range of 500Å to 1000Å.

30

12. A method of producing mirrors as defined in claim 11, wherein said protective layer comprises undoped tin oxide in a thickness range of 750Å to 1000Å.

5 13. A method of producing mirrors including depositing onto a ribbon of hot glass during the production process a coating comprising a first layer consisting essentially of silicon having a refractive index of at least 2.8 and a thickness in the range of 100Å  
10 to 300Å, a second layer consisting essentially of an oxide of silicon having a refractive index of less than 2 and a thickness in the range of 100Å to 400Å, and a third layer consisting essentially of an oxide selected from the group consisting of tin oxide, titanium oxide and mixtures  
15 thereof in a thickness range of 500Å to 1000Å, whereby the mirrors have a visible light reflectance between 35% and 60%, preferably between 35% and 55%, and a reflected color defined by the CIELAB color scale of a\* between -10, preferably between -15, and -25 and b\* between  
20 -15 and -30 (Illuminant A).

14. A method as defined in claim 13, wherein said second layer is in a thickness range of 200Å to 400Å, and said third layer is in a thickness range of 750Å to 1000Å.  
25

15. A method of producing automotive mirrors exhibiting a reflected color, including depositing onto a ribbon of hot glass during the production process a coating comprising at least one pyrolytic reflecting  
30 layer, a color modifying layer and a protective layer, annealing the coated ribbon, cutting the annealed ribbon into blanks, and thereafter bending said blanks to provide

mirrors having a visible light reflectance of less than 70% and a reflected color defined by the CIELAB color scale system of  $a^*$  between -10, preferably between -15, and -25 and  $b^*$  between -15 and -30 (Illuminant A).

5

16. A method as defined in claim 15, including the further step, subsequent to said bending, of tempering the bent blanks.

10

17. An automotive mirror comprising a float glass substrate carrying a coating including a first layer consisting essentially of silicon having a refractive index of at least 2.8 and a thickness in the range of 100Å to 300Å, a second layer consisting essentially of an oxide of silicon having a refractive index less than 2 and a thickness in the range of 100Å to 400Å, and a third layer consisting essentially of an oxide selected from the group consisting of tin oxide, titanium oxide and mixtures thereof in a thickness range of 500Å to 1000Å, said mirror having a visible light reflectance in the range of 35% to 60%, preferably, 35% to 55%, and a reflected color defined by the CIELAB color scale system of  $a^*$  between -10, preferably between -15, and -25 and  $b^*$  between -15 and -30 (Illuminant A).

25

30

18. A method of producing an automotive mirror including depositing onto a ribbon of hot glass during the production process a coating comprising at least one pyrolytic reflecting layer, annealing the coated ribbon  
5 cutting sheets of mirror glass from the coated ribbon, bending said mirror sheets to the required curvature and cutting said bent sheets to size for use as automotive mirrors.

10 19. A method as defined in claim 18, wherein the pyrolytic reflecting layer is a layer of silicon, tin oxide or titanium oxide.

20. A method as defined in claim 18, including  
15 additionally depositing at least one reflection enhancing layer on the hot glass during the production process.

21. A method as defined in claim 20, wherein a layer of silicon oxide is deposited as a reflection enhancing  
20 layer.

22. A method as defined in claim 18, including additionally depositing at least one color modifying layer on the hot glass during the production process.  
25

23. A method as defined in claim 22, wherein a layer of silicon oxide is deposited as a color modifying layer.

24. A method as defined in claim 20, wherein the  
30 mirror produced has a reflection color such that, when defined by reference to the CIELAB color scale,  $a^2 + b^2$  is not greater than 50.

25. A method as defined in claim 22, wherein the mirror produced has a reflection color such that, when defined by reference to the CIELAB color scale,  $a^2+b^2$  is greater than 50.

5

26. A method as defined in claim 18, wherein the reflecting layer is applied to a ribbon of float glass less than 3 mm, preferably less than 2.5 mm, thick.

10

27. A method of producing an automotive mirror including depositing onto a ribbon of hot glass during the production process a coating comprising at least one pyrolytic reflecting layer, annealing the coated ribbon, cutting the annealed ribbon into blanks and bending and thereafter tempering said blanks for use as automotive mirrors.

15

28. A method as defined in claim 27, wherein the pyrolytic reflecting layer is a layer of silicon, tin oxide or titanium oxide.

20

29. A method as defined in claim 27, including additionally depositing at least one reflection enhancing layer on the hot glass during the production process.

25

30. A method as defined in claim 29, including depositing a layer of silicon oxide as a reflection enhancing layer.

30

31. A method as defined in claim 27, including additionally depositing at least one color modifying layer on the hot glass during the production process.

21

32. A method as defined in claim 31, including depositing a layer of silicon oxide as a color modifying layer.

5        33. A method as defined in claim 29, wherein the mirror produced has a reflection color such that, when defined by reference to the CIELAB color scale,  $a^2+b^2$  is not greater than 50.

10       34. A method as defined in claim 31, wherein the mirror produced has a reflection color such that, when defined by reference to the CIELAB color scale,  $a^2+b^2$  is greater than 50.

15       35. A method as defined in claim 27, wherein the reflecting layer is applied to a ribbon of float glass less than 3 mm, preferably less than 2.5 mm, thick.

20

1/1

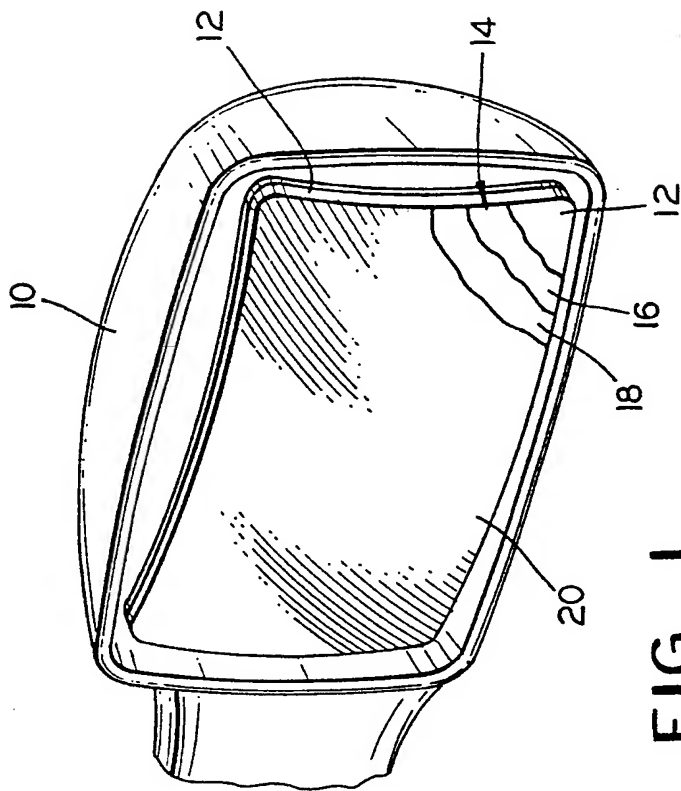


FIG. 1

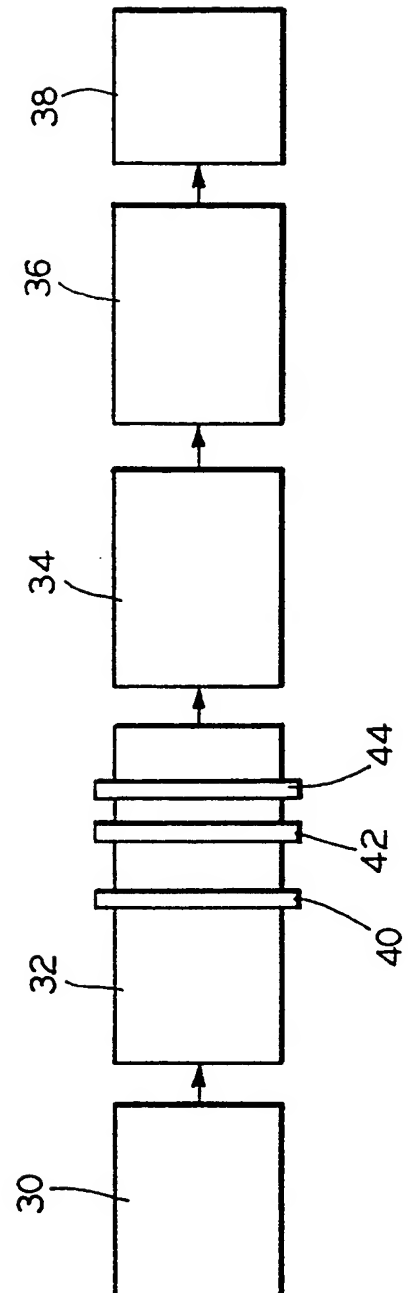


FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/00291

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C03C 17/34; C23C 16/22, 16/44; B05D 5/06; B23B 17/06

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 4,661,381 (CALLIES ET AL) 28 April 1987, see entire document and especially col. 3, line 67 to col. 4, line 15, col. 4, line 1.	1, 4 ----- 2-3, 5-35
Y	US, A, 5,267,081 (PEIN) 30 November 1993, see entire document.	1, 4, 18-23, 26-32, 35
Y	US, A, 4,188,444 (LANDAU) 12 February 1980, see entire document.	1, 4, 18-23, 26-32, 35
A	US, A, 4,847,157 (GOODMAN ET AL) 11 July 1989, see entire document.	1-35
A	US, A, 5,217,753 (GOODMAN ET AL) 08 June 1993, see entire document.	1-35

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

17 MARCH 1995

Date of mailing of the international search report

11 APR 1995

Name and mailing address of the ISA/US  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/00291

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,469,045 (CHESWORTH) 04 September 1984, see entire document.	1-35
A	US, A, 4,088,471 (KIRKBRIDE ET AL) 09 May 1978, see entire document.	1-35
A	US, A, 5,216,551 (FUJII) 01 June 1993, see entire document.	1-35
A	US, A, 5,203,903 (TERNEU ET AL) 20 April 1993, see entire document.	1-35
A	US, A, 4,419,386 (GORDON) 06 December 1983, see entire document.	1-35
A	Introduction to Ceramics, Second Edition, 1976, W.D. KINGERY ET AL, page 662.	6, 8, 13, 17

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/00291

## A. CLASSIFICATION OF SUBJECT MATTER: US CL :

65/60.2, 60.5, 60.8, 95, 97, 30.1; 427/167, 255, 419.3; 359/839, 586, 359; 428/428, 912.2

## B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

65/60.1, 60.2, 60.5, 60.53, 60.8, 95, 97, 99.1, 30.1, 30.11; 427/163.1, 165, 166, 167, 255, 419.3, 419.4, 419.6;  
359/839, 900, 586, 884, 359; 428/428, 426, 429, 912.2